Argonne National Laboratory

OUT-OF-PILE STUDY OF THE EFFECTS OF THERMAL GRADIENTS ON THE DISTRIBUTION OF PLUTONIUM IN FAST-REACTOR FUEL MATERIALS

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M. G. Chasanov and D. F. Fischer

ARGONNE NATIONAL LABORATORY
9700 South Cass Avenue
Argonne, Illinois 60439

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Chemical Engineering Division

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ABSTRACT

Annealing of ceria-urania and plutonia-urania pellets in thermal gradients resulted in apparent increases in cerium and plutonium concentrations at the hotter end of the samples. These results are discussed in terms of various possible mechanisms. Similar experiments on mixed-carbide samples indicated that vaporization losses of plutonium from the hotter end, although extensive under some conditions, can be minimized by the use of cladding.

I. INTRODUCTION

A frequent observation in mixed-oxide fuel specimens irradiated to burnups of several percent or higher is an increase in plutonium content in the columnar-grain region as the central-void region is approached. Migration and segregation of fissile and fertile materials within a fast-reactor fuel during its operational lifetime could have significant effects on the operational safety of the fuel if the magnitude of such separations were large. Redistribution of plutonium in $(U,Pu)O_2$ fuels might change the chemical and physical properties of the affected region enough to alter the neutronics of the system, affect fuel-cladding compatibility, and change the resultant fission-product distribution. The large thermal gradients existing in an operating oxide fuel pin are extremely important factors in determining the behavior of the fissile and fertile materials as well as of fission products produced during irradiation. The purpose of the study reported here was to examine the effects of thermal gradients on plutonium redistribution in fast-reactor fuel through a series of experiments that would be free of the effects of other variables; this was done in the out-of-pile work reported below.

II. EXPERIMENTAL APPARATUS

A furnace was developed that could maintain an axial temperature gradient of at least 1000°C/cm across a small fuel pellet in a plutonium glovebox. Thermal-gradient furnaces designed for use at high temperatures have usually used an electrically heated rod passed through the center of an annular solid sample.[1-3] Other experimenters have reversed this procedure by heating the periphery of an annular sample while cooling the inner surface.[4] However, these devices were used to produce radial gradients in the sample specimens. To produce an axial gradient in a small sample, Beisswenger et al.[5] electrically heated a tungsten tube which contained the sample; the bottom of the sample was maintained at a lower temperature by water-cooling. We developed a furnace utilizing radiant energy from a small, electrically heated tungsten foil placed directly over the sample specimen; the simplicity of this furnace makes it especially suitable for glovebox manipulations. An additional feature of our apparatus is the use of an oil-free vacuum system which is compact enough to be completely contained within the limited space available in a plutonium glovebox and which is virtually free of vibration.

The two main portions of the apparatus are the vacuum chamber and the gradient furnace (shown schematically in Figs. 1 and 2, respectively). The former is a modified Varian VI-10 stainless steel vacuum chamber with a molecular-sieve sorption pump for rough pumping and both a 15-liter/sec ion pump and a titanium sublimation pump for high vacuum. The vacuum chamber is 12 in. in diameter and 9 in. high. A 14-in.-diam base plate rests on a Viton O-ring at the top of the vacuum-chamber flange. A 5-in.-diam opening through the center of the base plate accommodates the thermal-gradient furnace. A 6-in.-diam stainless steel bell jar surrounds the furnace components and is sealed with an L-shaped Viton boot to the top of the base plate. All the electrical power supplies and controls are located outside the box.

In Fig. 2, the heating element for the furnace is an electrically heated 5-mil tungsten foil, 0.75 in. wide and approximately 3 in. long. Each end of the heating element is clamped within a water-cooled copper block, which serves as an electrical terminal. The power supply for the heating element is a 12-V, 750-A transformer controlled by an autotransformer that connects to a 440-V, 20-A, single-phase line. The top window of the glovebox was modified by installation of metal gloveport plugs. Electrical power for the furnace is brought into the glovebox through MI cables, which have insulating fittings mounted on a metal gloveport plug in the top window.
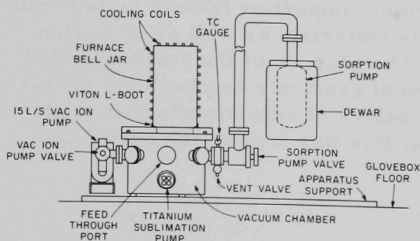
Fig. 1. Gradient-furnace Vacuum System Contained in Plutonium Glovebox. ANL Neg. No. 308-209 Rev. 1.

Cables from these fittings lead to the water-cooled power feedthroughs on the vacuum chamber. MI cable has one or more electrical conductors insulated with a highly compressed refractory mineral insulation and enclosed in a gas-tight tube sheathing. In our case, the conductors and sheathing are electrolytic copper and the insulation is magnesium oxide.
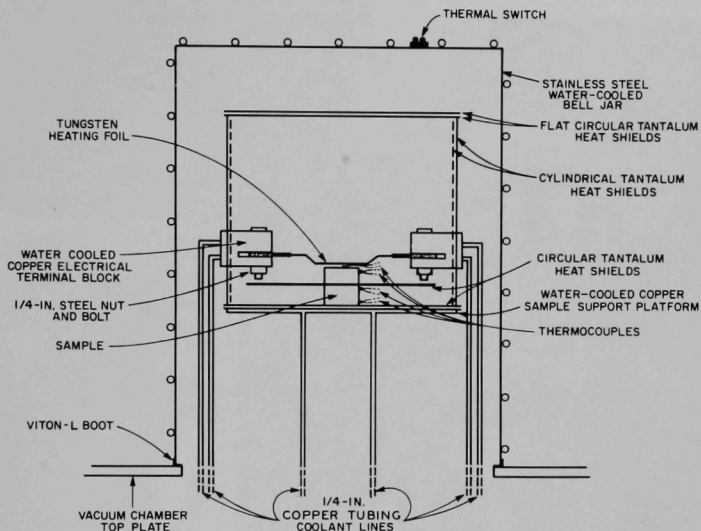
Fig. 2. Schematic Drawing of Thermal-gradient Furnace in Position inside the Bell Jar. ANL Neg. No. 308-662 Rev. 2.

Figure 3 is a photograph of the apparatus in the glovebox and the control equipment associated with it; this photograph was made before final closing of the glovebox. As shown in the figure, most of the control equipment for the system was located outside the glovebox.

The fuel pellet, typically a cylindrical specimen about 0.5 in. in both diameter and height, is positioned approximately 0.5 to 1 mm below the heating element. The fuel pellet rests on a tantalum foil in contact with a water-cooled copper support platform. A tantalum heat shield, supported on small tabs spot-welded to the underside of the shield, is situated around the pellet at its midplane. Thermocouples are positioned in the pellet before placing two cylindrical tantalum heat shields and covers around the furnace.

The thermocouples used for these studies were of tungsten-5% rhenium/tungsten-26% rhenium; the materials used were of 5-mil-diam wire manufactured by Hoskins Manufacturing Co., Detroit, Michigan. The emf's produced by the thermocouples were recorded on a Brown 12-point

recorder. The voltages were converted to temperatures using the emf-temperature equation of Novak and Asamoto;[6] the accuracy requirements of the experiments did not warrant individual calibration of the thermocouples. Figure 4 shows the thermocouples in place in the sample and the thermocouple leads in the apparatus.
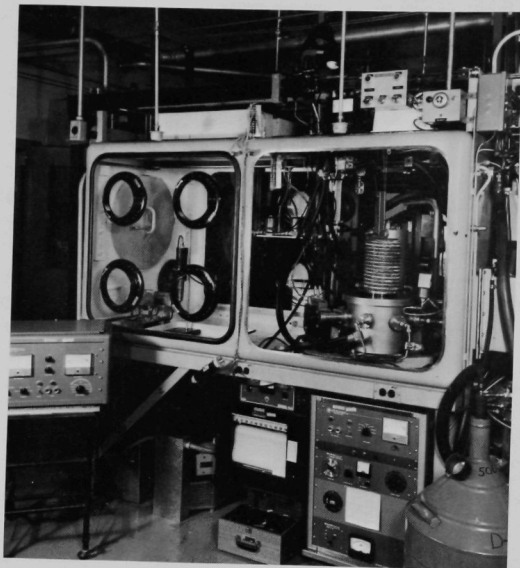
Fig. 3

Thermal-gradient Apparatus Installed in Plutonium Glovebox. ANL Neg. No. 308-538.
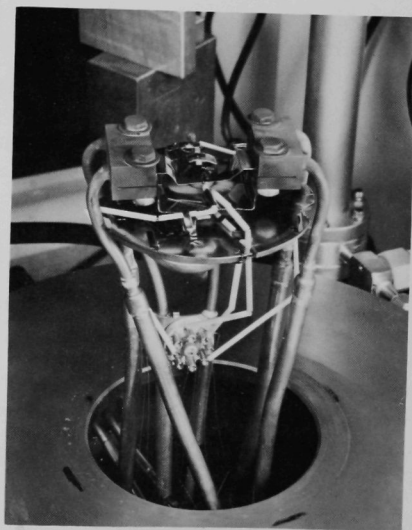
Fig. 4

Photograph of Sample Positioned in Furnace with Thermocouples in Place. ANL Neg. No. 308-532.

Samples were drilled for positioning the thermocouples employing an ultrasonic generator using for a drill a small hypodermic needle. The sample was held manually in a small plastic bag containing boron carbide and trichloroethylene as a cutting liquid. The drilling apparatus is shown in Fig. 5, along with the cutting wheel used to section samples mounted for ceramographic and electron-microprobe examination.

The samples were prepared for ceramographic examination with the usual polishing techniques. Those destined for electron-microprobe analysis were mounted using a copper-bakelite compound, and a thin layer of nickel was vapor-deposited to reduce the hazards of loose surface activity.

Fig. 5. Ultrasonic Drilling Apparatus and Cutting Wheel Used in Plutonium Glovebox. ANL Neg. No. 308-534.

III. CeO_2-UO_2 STUDIES

Cerium is an important fission product and its oxide, CeO_2, has often been used as a stand-in for PuO_2 in fuel-simulation studies. As a test of the operation of the system before engaging in the plutonium studies and also to obtain some information on this significant fission-product oxide, a preliminary series of experiments was carried out in the thermal-gradient apparatus previously described.

A. Materials

CeO_2-UO_2 solid-solution samples were fabricated from a mechanical mixture in the form of 3/8-in.-diam by 1/2-in.-long pellets by the Materials Science Division at ANL. Two ceria-urania compositions were used in these studies: nominally $(U_{0.85}Ce_{0.15})O_2$ and nominally $(U_{0.70}Ce_{0.30})O_2$. The actual compositions of these materials are given in Table I; in the subsequent discussion the materials will be referred to in terms of their actual initial cerium content in weight percent rather than nominal mole percent of ceria. The compositions computed from the analytical data for the nominal 30 mol % ceria-urania material (assuming the oxygen and cerium data to be correct and obtaining the uranium by difference) is $(U_{0.78}Ce_{0.22})O_{2.007}$. Most

experiments were done with this material. An independent oxygen analysis was not obtained for the nominally 15 mol % ceria pellets; however, it is believed that the oxygen-to-metal ratio was slightly hyperstoichiometric.

TABLE I. Composition of Ceria-Urania Solid-solution Pellets
Used in Thermal-gradient Experiments

Nominal Composition	wt % Ce[a]	wt % U[a]	wt % O[b]
$(U_{0.85}Ce_{0.15})O_2$	8.4	79	-
$(U_{0.70}Ce_{0.30})O_2$	12.4	76	12.9

[a]Determined by colorimetric analysis.
[b]Determined by vacuum fusion.

B. Experimental Results

The results of experiments in which samples were heated in the thermal-gradient furnace for extended periods indicated significant loss of material through vaporization processes. The upper-surface temperature for the samples was about 2000°C. Table II gives the weight-loss data obtained for studies in which the system was back-filled with about 150 Torr of argon. An experiment in which the sample had a vapor-deposited 9-mil tungsten coating gave much-reduced losses.

TABLE II. Weight-loss Data for Thermal-gradient Experiments
with Ceria-Urania Pellets

Cerium Content, wt %	Heating Time, hr	Thermal Gradient,[a] °C/cm	Total Weight Loss, wt %
8.4	100	1100	4.1
8.4	514	890[b]	3.8
12.4	100	1050	3.4
12.4	504	1060	14
12.4 (9-mil W clad)	500	920	0.25

[a]The temperature at the top of the pellet was approximately 2000°C.
[b]Lower gradient due to changed heat-shield geometry.

Ceramographic examination of the heated pellets revealed that pore migration toward the hotter end of the samples had taken place. Figure 6 is a longitudinal cross section of the pellet containing 12.4 wt % cerium

that had been heated for 100 hr in a gradient of about 1050°C/cm. The increase in porosity near the top of the sample is quite evident in the figure; unheated samples show a more uniform distribution of pores and, in general, pores of a much smaller size. Associated with the porous region near the top of the sample are evidences of columnar-grain growth. Figure 7 shows a portion of the longitudinal cross section near the top of the pellet containing 12.4 wt % cerium which had been heated for 504 hr. A portion of the central part of the same heated pellet is also shown for comparison. The difference in porosity and grain size is quite evident.

Table II indicates significant loss of material through evaporation from the unclad heated pellets. Deposits of material were found on the outer periphery of the pellets; these whisker-like growths contained uranium, cerium, and small amounts of tungsten. X-ray examination of these single-phase materials gave the same type structure (fcc) as the original pellet, but the lattice parameters corresponded to a somewhat more uranium-rich solid solution. The lattice parameter for whisker material

Fig. 6. Longitudinal Cross Section of a Urania-Ceria Pellet (12.4 wt % cerium) Heated in Thermal Gradient of 1050°C/cm for 100 hr. ANL Neg. No. 308-563.
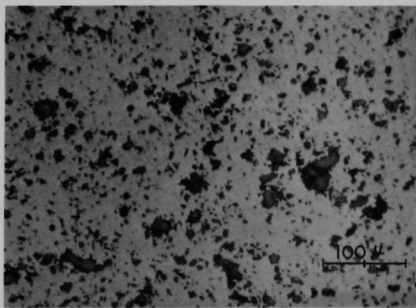
Top Portion   Central Portion

Fig. 7. Longitudinal Cross Section of a Urania-Ceria Pellet (12.4 wt % cerium) Heated in Thermal Gradient of 1060°C/cm for 504 hr. ANL Neg. No. 308-565.

from 12.4 wt % cerium material heated for 100 hr was 5.460 ± 0.003 Å.
From Vegard's law, this would correspond to 9.6 wt % cerium; however,
spectrochemical analysis of the same sample gave a composition correspond-
ing to 12.2 wt % cerium, which is probably the more correct value. The
lattice parameter for the growth from a pellet of that same initial composi-
tion heated in a gradient for 504 hr was 5.464 ± 0.003 Å, which corresponds
(by Vegard's law) to a composition of 8.1 wt % cerium. Whisker growth was
insignificant in the case of the clad pellet. However, the clad pellet displayed
rather extensive cracking and increased porosity in the latter regions of the
sample.

An experiment in which a pellet containing 12.4 wt % cerium was
heated at a higher temperature (surface ~2300°C) for 93 hr yielded a gradient
of about 1310°C/cm. This specimen on ceramographic examination showed
columnar-grain growth in the upper heated regions.

The above ceria-urania samples were submitted for electron micro-
probe analysis for cerium and uranium. Longitudinal sections of the pellets
were scanned along the centerline using standard microprobe techniques.
The Ce/U counting ratios, obtained from the electron-microprobe scans
using a defocused electron beam of about 50-μm diameter, were employed to
calculate cerium and uranium concentration profiles as a function of distance
from the cooler end of the pellet; these profiles are presented in Figs. 8
and 9. The degree of initial inhomogeneity in these pellets would mask small
composition changes of the order of 0.5 wt % cerium.

Fig. 8. Cerium Distribution in $(U,Ce)O_2$ Pellets after
Heating in Thermal-gradient Furnace; Initial
Cerium Content: 8.4 wt %. ANL Neg.
No. 308-786 Rev. 1.
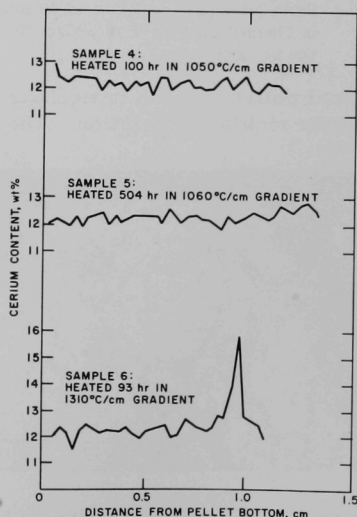
Fig. 9. Cerium Distribution in $(U,Ce)O_2$ Pellets after
Heating in Thermal-gradient Furnace; Initial
Cerium Content: 12.4 wt %. ANL Neg.
No. 308-787 Rev. 1.

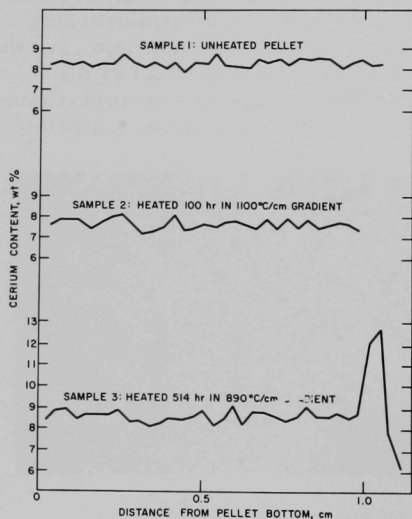The comparison of the cerium concentration profiles in Fig. 8 for pellets containing 8.4 wt % cerium initially showed no distinguishable change in cerium content for a sample (No. 2) heated 100 hr in an 1100°C/cm gradient, although a sample (No. 3) heated 514 hr in a somewhat smaller gradient (890°C/cm) showed a maximum in cerium content near the hotter end of the sample. Ceramographic examination of sample 3 revealed a horizontal crack near the hotter end and a porous region followed by a columnar-grain region in the vicinity of the cerium maximum.

Figure 9 compares cerium concentration profiles for three heated pellets, initially containing 12.4 wt % cerium. For sample 4, heated 100 hr in a 1050°C/cm gradient, no significant concentration change was observed. Sample 5, heated 500 hr in a 1060°C/cm gradient, exhibited no cerium-concentration peaks, although a trend toward higher concentration at the hotter end of the pellet exists. An interesting feature of the latter sample is that the trend toward higher cerium concentrations is associated with a region of porosity and columnar grains; however, no major horizontal cracks were observed. For sample 6, heated for 93 hr in a larger thermal gradient (1310°C/cm), a cerium-concentration peak was observed; a horizontal crack was noted near the bottom end, and columnar grains began in the sample near the area designated by the peak in the curve.

Radial microprobe traverses across these pellets in the bottom, center, and top regions revealed no significant radial variations in composition after heating in the thermal-gradient furnace.

Thus, in these experiments, apparent migration of cerium toward the hotter end of the specimen was observed; Beisswenger et al.,[5] also observed such cerium-concentration enhancement in their studies of the effects of thermal gradients on the ceria-urania system. They attributed this effect to thermal diffusion; in our experiments, it is not clear that such was necessarily the case. The general occurrence of cracks, pores, and columnar grains, in association with the observed cerium-concentration maxima, imply that a vapor-transport process, possibly involved with pore sweeping, might be an appropriate mechanism.

The above studies on the ceria-urania system established that our apparatus was reliable enough to operate in a glovebox. These preliminary tests were terminated and the apparatus installed in the plutonium glovebox (see Fig. 3).

IV. PuO_2-UO_2 STUDIES

The fuel that has been decided upon for LMFBR development is the plutonia-urania mixed oxide. Our thermal-gradient studies were performed on the 20 mol % plutonia-urania composition, this being the composition of reactor interest at the time the studies were carried out. It was originally planned to study the effects of plutonium concentration, O/M ratio, and

pellet density on the redistribution of plutonium in a thermal gradient; not all these plans were accomplished.

A. Materials

The samples used in these studies were cylindrical pellets half an inch in both diameter and height. They were prepared from coprecipitated solid-solution material by Nuclear Materials and Equipment Corporation (NUMEC) in two batches. Depleted uranium was used in both batches of pellets. The average density of the first batch of material was 10.59 g/cm^3; that of the second batch was 10.69 g/cm^3. The O/M ratio of the first batch was 2.01 and the plutonium content was 18.01 wt %; the second batch had an O/M ratio of 1.97 and the slightly lower plutonium content of 17.26 wt %. Both compositions correspond to about 20 wt % plutonia. Chemical analysis of impurities in the pellets is given in Table III. Ceramographic examination of the pellets indicated they consisted of high-density single-phase material with relatively fine grain size.

TABLE III. Chemical Analysis of 20 wt % PuO_2-UO_2 Pellets
Supplied by NUMEC

Impurity	Concentration, ppm		Impurity	Concentration, ppm	
	Batch 1	Batch 2		Batch 1	Batch 2
Cd	<1	<1	Sn	1	<10
B	<1	<1	V	<1	<1
Mn	1	25	Cu	1	8
Mg	4	3	Ti	<1	<1
Pb	<10	<10	Co	<1	<1
Si	<20	<20	Bi	<10	<10
Fe	<10	75	Be	<1	<1
Cr	<10	60	Zr	<50	<50
Ni	<20	10	Ca	<100	<100
Al	<20	<20	Na	-	<100
Mo	5	<10			

B. Experimental Results

The experimental procedure and analytical techniques used with the plutonia-urania experiments were identical to those employed in the ceria-urania studies. The bell-jar system after evacuation was back-filled with a few hundred Torr of high-purity argon to reduce vaporization from these samples. During the studies, vaporization losses were reduced markedly (as in the case of the ceria-urania experiments) by use of a metal cladding. For use with the plutonia-urania pellets, small tungsten crucibles were prepared by vapor deposition and thermocouple holes made in them by

electrical-discharge machining; these crucibles were inverted and the samples covered with them. Figure 10 is a schematic drawing of the crucibles employed in these studies.
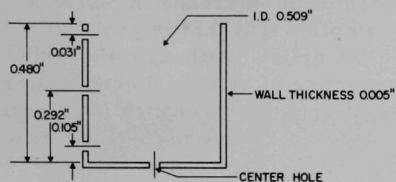
Fig. 10. Tungsten Crucible Used as Vaporization Barrier in Mixed-oxide Experiments. ANL Neg. No. 308-2286.

The samples were analyzed for uranium and plutonium on longitudinally sectioned pellets using the electron microprobe. Ceramographic examination and alpha autoradiography were also employed with these samples.

Table IV reports the results obtained in studies involving the slightly hyperstoichiometric mixed-oxide specimens. Those cases in which no significant plutonium redistribution were observed (samples 1 through 4) are characterized by variation of plutonia content by no more than ±0.5 wt % plutonia from the mean composition. Samples 5 and 8 did show an increase in plutonium content at the hotter end of the sample; the magnitudes of the increases were such that it appeared unlikely that they were due to initial inhomogeneities in the specimen before heating. Figures 11 and 12 show

TABLE IV. Summary of Thermal-gradient Experiments with $(U_{0.8}Pu_{0.2})O_{2.01}$ Pellets

Sample No.	Duration, hr	Top Temp, °C	Bottom Temp, °C	Results of Electron-microprobe Analysis
1[a]	100	1980	1280	No plutonium redistribution
2	100	2070	975	No plutonium redistribution
3[a]	500	1980	1250	No plutonium redistribution
4	504	2040	960	No significant plutonium redistribution
5[a]	1020	1970	1140	Apparent plutonium increase at hotter end
8[a]	123	2340	1220	Apparent plutonium increase at hotter end

[a]The sample was contained in an inverted metal crucible fabricated from 5-mil tungsten; this served as a barrier to loss of material by evaporation.
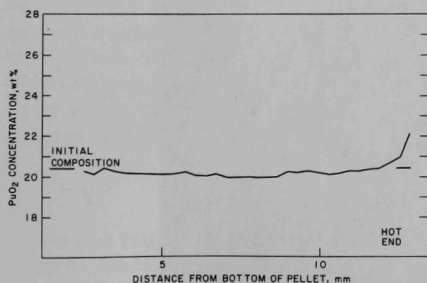
Fig. 11. Plutonia Distribution along Centerline of $(U_{0.8}Pu_{0.2})O_{2.01}$ Pellet (sample 5) Heated 1020 hr in Thermal-gradient Apparatus ($T_{top} = 1970°C$, $T_{bottom} = 1140°C$). ANL Neg. No. 308-1770.
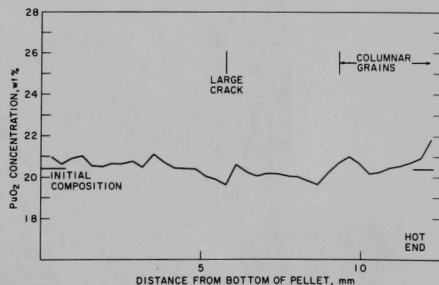
Fig. 12. Plutonia Distribution along Centerline of $(U_{0.8}Pu_{0.2})O_{2.01}$ Pellet (sample 8) Heated 123 hr in Thermal-gradient Apparatus ($T_{top} = 2340°C$, $T_{bottom} = 1220°C$). ANL Neg. No. 308-1768.

the variation of plutonia concentration in samples 5 and 8 (as computed from the electron-microprobe data) as a function of distance from the bottom of the pellet. The relative smoothness of the increase in plutonia concentration at the hotter end of sample 5 implies that this is probably not due to segregation originally present in the pellet. Although the variations in plutonia concentration along the centerline of sample 8 are greater than those observed in pellet 5 (this can be attributed to a change in mounting material used in sample preparation), the increase in plutonia concentration at the hotter end is still quite evident.

The magnitude of the increases observed are relatively small (10% relative increase), and the time required at T_{top} ~2000°C was relatively long; experiments at higher temperatures, such as T_{top} of 2340°C for sample 8, were difficult because of short heating-foil lifetime (~14 hr). However, a longer-term experiment (432 hr) was performed at this higher temperature. Vaporization processes resulted in significant losses of material from the upper portions of the sample, and no plutonia-concentration change was observed.

Ceramographic examination of the mixed-oxide specimens usually revealed significant cracking; however, it is not clear whether this was the result of thermal shock, cladding restraint, or mounting the specimens in the copper bakelite compound used for most of the microprobe analyses. Sample 5 showed clear-cut evidence of the growth of columnar grains at the upper (hotter) surface; Fig. 13 shows the columnar-grain region in this specimen, which had been heated for 1020 hr. The pores in upper

Fig. 13. Columnar-grain Growth in Mixed-oxide Sample 5 Heated in 1020 hr in Thermal-gradient Apparatus (T_{top} = 1970°C, T_{bottom} = 1140°C). ANL Neg. No. 308-2278.

portion of the sample were significantly larger than those in the central or lower portions of the specimen. In addition, the pores in the upper region of the pellet frequently had a lenticular shape (see Fig. 14). Sample 8 showed the same type of columnar-grain growth and pore distribution as sample 5.

Fig. 14

Pores in Upper Region of Mixed-oxide Sample 8 Heated 123 hr in Thermal-gradient Apparatus (T_{top} = 2340°C, T_{bottom} = 1220°C). ANL Neg. No. 308-2281.

Although all the above samples heated in the tungsten crucible showed some growth of whisker material at the crucible surface, sample 4 (heated 500 hr without the tungsten crucible) displayed a very large amount of this growth. Figure 15 is a photograph of this pellet, after the experiment, next to an unheated specimen. A sample of material from the outer edge of the growth region had a face-centered-cubic structure with a lattice parameter of 5.468 Å; material from the growth region just above the pellet's lateral surface had a lattice parameter of 5.472 Å. These parameters would correspond to very low plutonia-content materials for near-stoichiometric mixed oxides.

Fig. 15

Growth on Mixed-oxide Sample 4 after Heating for 504 hr in Thermal-gradient Furnace with No Tungsten Vaporization Barrier (T_{top} = 2040°C, T_{bottom} = 960°C). Second pellet is unheated specimen from same batch. ANL Neg. No. 308-2279.
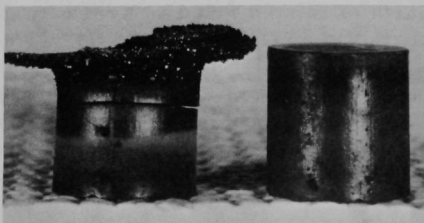
Alpha autoradiography was not very informative in the above studies, since the variations in plutonia concentration were relatively small.

Experiments with oxide materials from the second batch of pellets, slightly hypostoichiometric, were performed in the same apparatus using the tungsten crucibles as vaporization barriers. The results of these experiments are given in Table V. For sample 12 (little vaporization of the upper region of the pellet), the centerline concentration of plutonia was analyzed to be 19.8 mol % with a standard deviation of 0.3 mol %. Thus, under conditions that had produced an apparent enhancement of plutonium content at the hot end of a hyperstoichiometric pellet, a similar effect was not observed for this hypostoichiometric material.

TABLE V. Summary of Thermal-gradient Experiments with $(U_{0.8}Pu_{0.2})O_{1.97}$ Pellets

Sample No.	Duration, hr	Top Temp, °C	Bottom Temp, °C	Results of Electron-microprobe Analysis
10[a]	262	2360	1160	Vaporization of region of interest
11[a]	93	2350	1180	Vaporization of region of interest
12	125	2360	1310	No plutonium redistribution

[a]No plutonium redistribution observed in the unvaporized portion of pellet (about 81% of original length at centerline).

In all the above mixed-oxide studies, radial electron-microprobe scans were made on a routine basis and no marked radial variations in plutonia concentrations were observed.

Oxygen analyses were performed by vacuum fusion on samples (~0.3 g in weight) cut from several of the heated pellets. These showed the expected trend--a marked decrease in oxygen content in the hotter portions of the pellets. In addition, there was an overall loss of oxygen from the pellets, the losses being larger for pellets that were heated for longer periods and held at higher temperatures. A sample from the top fourth of sample 5 had an O/M ratio of 1.92, whereas one from the bottom fourth had an O/M ratio of 1.94. (The initial O/M ratio of the unheated pellets was 2.01.) For sample 8, heated at much higher temperatures, the O/M ratio was 1.81 for the top region and 1.92 for the bottom region. The O/M ratios in the heated pellets appeared to vary smoothly from the top to the bottom of the pellet. However, the data are too limited to draw firm conclusions as to oxygen behavior in the system.

V. MIXED-CARBIDE FUELS

Mixed-carbide fuel materials, because of their excellent heat-transfer properties, are of significant interest for fuels as fast breeder reactors. Only few scouting studies of the effects of a thermal gradient on such materials were carried out; the experiments performed are reported below.

A. Materials

Fluid-bed preparation of the mixed-carbide material was performed in the Chemical Engineering Division at ANL. Pellets were then pressed from these materials at 38,000 psi and sintered at 2100°C; the resultant fired cylindrical pellets were 0.43 in. in diameter and 0.42 in. long. The composition of these pellets was: 80.99 wt % uranium, 14.4 wt % plutonium, and 4.61 wt % carbon; this corresponds to $(U_{0.85}Pu_{0.15})C_{0.96}$.

B. Experimental Results

The mixed-carbide pellets were somewhat smaller than the mixed-oxide specimens; thus new tungsten crucibles had to be fabricated for use with the carbides. Several preliminary tests were made without the use of the crucibles. Sample 13 was heated for 100 hr in the thermal-gradient apparatus (T_{top} = 1990°C, T_{bottom} = 1390°C). This specimen, on removal from the furnace, revealed marked swelling of the top fourth of the pellet (see Fig. 16); the top surface had a crusty layer, under which was a granular material. The X-ray parameter of material from the crusty layer was 4.952 Å; that of the granular material was 4.953 Å. The patterns were typical of mixed carbides, but these lattice parameters were substantially smaller.

A similar pellet (sample 14) was annealed in the apparatus without a tungsten crucible for 437 hr (T_{top} = 1980°C, T_{bottom} = 1370°C). The swelling observed in sample 13 did not occur in this case; however, vaporization losses were more significant (a weight loss of 2.7% for sample 14 versus 0.87% for sample 13).

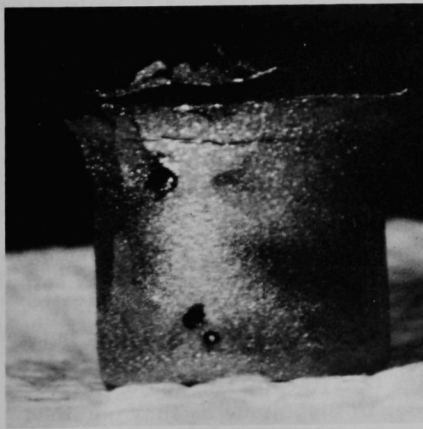Sample 16, a similar carbide pellet, was annealed in the apparatus

Fig. 16. $(U_{0.85}Pu_{0.15})C_{0.96}$ Pellet (sample 13) after 100 hr in Thermal-gradient Furnace (T_{top} = 1990°C, T_{bottom} = 1390°C). ANL Neg. No. 308-2280.

using a tungsten crucible whose top thermocouple hole was covered with a piece of tungsten sheet; this was done to reduce vaporization losses. The specimen was heated for 460 hr (T_{top} = 2050°C, T_{bottom} = 1320°C). Sample losses by vaporization, as indicated by weighing and ceramography, were minimal.

Samples 14 and 16 were submitted for plutonium and uranium analysis using the electron microprobe; scans were performed along the longitudinal axis of the pellet in the usual fashion. The results indicated marked plutonium losses from the upper third of sample 14 (decreasing continuously from the initial composition to about 2 wt % plutonium near the top surface); sample 16 (heated in the tungsten crucible), on the other hand, revealed no significant composition changes.

Ceramographic examination of samples 14 and 16 revealed quite different behavior. The upper third of sample 14 comprised large, relatively pore-free, equiaxed and columnar grains. Most of the pores were quite large compared to the pores in the remainder of the sample. Sample 16 did not display the marked densification that distinguished sample 14; however, the upper regions of sample 16 were characterized by somewhat larger equiaxed grains than those in the rest of the specimen.

The electron-microprobe results for these two samples are not surprising, since it is well known that the chief high-temperature vapor species over such mixed carbides is plutonium. Unimpeded surface vaporization, along with pore movement in the thermal gradient, probably explains the results obtained with sample 14.

VI. DISCUSSION

A. Thermal Diffusion in Oxide Specimens

The redistribution of cerium in ceria-urania mixtures and of plutonium in plutonia-urania has been discussed by Beisswenger et al.;[5,7] nuclear-reactor implications of this treatment have also been considered by Wirtz.[8] Beisswenger et al.[7] observed that in a mixed-oxide fuel sample held in a thermal gradient (T_{max} = 2300°C) for 110 hr, a very small increase in PuO_2 concentration (about 5% relative) occurred at the hot end of the sample. Their treatment of this data was in terms of a thermal-diffusion mechanism resulting in a value of α (thermal-diffusion factor) of 11; this value of α had the same order of magnitude as they obtained in their ceria-urania studies.[5]

We followed the method employed by Beisswenger et al.[7] in treating our data for those mixed-oxide samples in which there was apparent redistribution of plutonium (samples 5 and 8). A brief outline of the method is given below; for more details, see Refs. 5 and 7.

The flux of component 1 in a thermal gradient is given by

$$J_1 = -D\nabla C_1 + D' \frac{C_1 C_2}{C_1 + C_2} \nabla T, \tag{1}$$

where

C_1 = concentration of component 1,

C_2 = concentration of component 2,

D = diffusion coefficient (cm^2/sec),

and

D' = thermal-diffusion coefficient $(cm^2/sec°K)$.

This, for a fixed lattice reference system, can be transformed to

$$J_1 = -D\left[\left(1 + \frac{C_1}{C_2}\right)\nabla C_1 - \frac{\alpha}{T} C_1 \nabla T\right], \tag{2}$$

where α is the thermal-diffusion factor $[\alpha = (D'/D) T]$. For D, we can employ the equation

$$D = D_0 \exp \frac{-Q}{RT}. \tag{3}$$

Substituting in Eq. 2, we obtain as the final equation

$$J_1 = -D_0\left[\left(1 + \frac{C_1}{C_2}\right)\nabla C_1 - \frac{\alpha}{T} C_1 \nabla T\right] \exp \frac{-Q}{RT}. \tag{4}$$

Employing Eq. 4 with the conservation-of-mass equation

$$\nabla \cdot J_1 + \frac{\partial C_1}{\partial t} = 0, \tag{5}$$

we can obtain computer solutions of C_1 as a function of time and axial position in the thermal gradient. These equations were solved for C_1 at fixed axial positions along the pellet using the algorithm

$$C_1(\zeta, t + \Delta T) = C_1(\zeta, t) - (\nabla \cdot J_1) \Delta t. \tag{6}$$

Various values of α were employed to obtain a satisfactory fit to the experimental data.

For the diffusion constant and activation energy of diffusion, the same values as used by Beisswenger et al.[7] were employed:

$$D_0 = 0.046 \text{ cm}^2/\text{sec};$$

$$Q = 100 \text{ kcal/mole}.$$

These values were based on the experimental data of Davis and Novak[9] and Schmitz and Lindner.[10]

The temperature distribution within the pellet is also a necessary input for the computation. The temperatures were measured at points in the pellet, as indicated in Fig. 10; however, these are effectively surface temperatures of the sample. These measured temperatures were plotted as a function of pellet height and fitted to a smooth curve by inspection. Temperatures read from this curve, coupled with the assumption of uniform top and bottom surface temperatures, were used in conjunction with an iterative computer program which solved the Laplace equation, $\nabla^2 T = 0$. From these computations, a radial and axial temperature map was obtained and the resultant centerline temperatures were used in the thermal-diffusion computations. All the above calculations were carried out on the CDC 3600 computer.

The results of fitting the thermal-diffusion equation to the maximum plutonium concentration in samples 5 and 8 gave values of α of 210 for sample 5 and 35 for sample 8; these values are in poor agreement with each other and also with Beisswenger et al.'s[7] value of 11. Figure 17 is a comparison of the data and the fit for sample 8. The markedly different values obtained from the experiments may indicate that the thermal-diffusion model does not truly represent the major process involved in producing the apparent plutonium maxima obtained by us and by Beisswenger et al. Although these equations may serve as a suitable correlative technique for individual experiments, it would appear that extrapolations using these values of α for longer-term annealing periods or for larger gradients could yield erroneous estimates of the degree of plutonium redistribution.

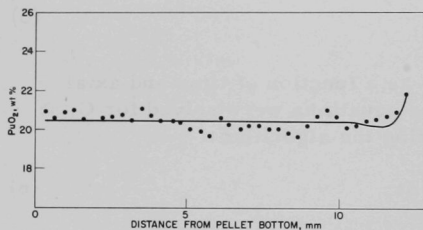Fig. 17. Thermal-diffusion Equation Fitted to Experimental PuO_2 Distribution along Axis of Mixed-oxide Sample 8. ANL Neg. No. 308-2285 Rev. 1.

B. Selective Vaporization Processes in Mixed Oxides

Rand and Markin[11] pointed out that, based on their calculations, vaporizing species over mixed oxides would be strongly dependent on stoichiometry of the condensed phase. For specimens at 2000°K, they

indicate that the UO_3 pressure increases rapidly as the composition passes through MO_2, and thus the vapor from hyperstoichiometric oxides is richer in uranium than the solid.

Recent experimental confirmation of this behavior can be found in the mass-spectrometric studies of $(U_{0.8}Pu_{0.2})O_{2-x}$ at 2240°K conducted by Battles and Blackburn.[12] These data show a significant increase in UO_3 pressure over the mixed oxide as the stoichiometric composition is approached. Blackburn[13] calculated that at 2000°C the pseudocongruent vaporization composition would be about $(U_{0.78}Pu_{0.22})O_{1.93}$; this is in reasonably good agreement with the results for sample 5.

Thus, if a process that depletes the specimen in uranium, through selective vaporization of UO_3, were to operate in a slightly hyperstoichiometric mixed-oxide pellet, one would expect to see an apparent increase in plutonium concentration in the affected region. However, for slightly hypostoichiometric samples, the total vaporization rate is reduced, UO_3 is no longer the most important vapor species, and little effect on plutonium concentration would be expected in the annealing times used on our experiments. These predictions, of course, are in agreement with our experimental observations. Although this does not prove that such vaporization accounts for the apparent plutonium redistribution in our work, it does imply that such a process could indeed have been operative in our studies. Bober et al.[14] have proposed a like mechanism to explain some of their observations. An interesting area for future investigation would be the effect of density on the extent of redistribution of plutonium in similar specimens.

C. Normal Freezing of Molten Fuels as a Mechanism for Plutonium Redistribution

Although some instances of enhanced plutonium concentration in operating fuel rods have occurred under circumstances where no fuel could have melted, there are other instances where melting could or did occur at some point in the fuel's lifetime.[15] Such melting of the fuel and its subsequent freezing could result in significant plutonium redistribution; this can result from zone refining by the solidus-liquidus separation effect--"normal freezing." Consider the case of a cylindrical fuel rod of unit height and radius R, which is solidifying inwardly; assume no solid diffusion and uniform concentration in the liquid. Given:

C = concentration of solute in solid at radius r,

K = distribution coefficient = C/C_ℓ,

C_ℓ = concentration of solute in liquid,

and

S = amount of solute in liquid.

We observe that

$$C = KC_\ell \tag{7}$$

and

$$C_\ell = \frac{S}{\pi r^2}. \tag{8}$$

Hence,

$$C = \frac{KS}{\pi r^2}. \tag{9}$$

Let us consider an annulus of the cylinder at radius r:

mass balance equation $\quad 2\pi r C \, dr = dS;$ \hfill (10)

if $dr < 0$, then $dS < 0$ (solidification);

if $dr > 0$, then $dS > 0$ (melting).

From Eqs. 9 and 10, we obtain

$$\frac{dS}{dr} = 2\pi r C = \frac{2KS}{r}. \tag{11}$$

Integrating Eq. 11 produces

$$\int_{S_0}^{S} d \ln S = 2K \int_{R}^{r} d \ln r$$

and leads to the relation

$$S/S_0 = \left(\frac{r}{R}\right)^{2K}. \tag{12}$$

Since $S_0 = \pi R^2 C_0$, we obtain

$$S = \pi R^2 C_0 \left(\frac{r}{R}\right)^{2K}. \tag{13}$$

Furthermore,

$$C = \frac{K}{\pi r^2}\left[\pi R^2 C_0\left(\frac{r}{R}\right)^{2K}\right] = K C_0 \left(\frac{r^2}{R^2}\right)^{K-1}. \tag{14}$$

If q is the fraction frozen, then

$$q = 1 - \frac{r^2}{R^2} \qquad (15)$$

and

$$C = KC_0(1 - q)^{K-1}. \qquad (16)$$

Equation 6 is the result obtained by Pfann.[16]

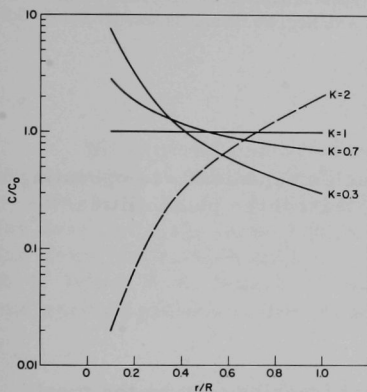
Fig. 18. Concentration Variation in a Normally Freezing Cylinder as a Function of Radius. ANL Neg. No. 308-2284.

Figure 18 indicates that if K < 1 the concentration in the resultant solid can increase as r decreases; the reverse will occur for K > 1. The phase diagram[17] for UO_2-20% PuO_2 indicates K ≃ 0.7 and enrichment of PuO_2 in the central region of a once-molten fuel rod should be expected to occur.

As an example, consider an irradiated mixed-oxide fuel described in detail by Brown et al.[18] The specimen was a vibratorily compacted hyperstoichiometric Dynapac powder rod of UO_2-20 wt % PuO_2 clad in Type 304 stainless steel (21 mils thick). The inner diameter of the cladding was 0.254 in.; the effective density of the $11\frac{3}{4}$-in.-long fuel rod was 83.5%. The specimen was irradiated in EBR-II for 119 days at 45 MW to a burnup of 2.9 at. % (6 x 10^{20} fissions/cm^3). The specimen after irradiation had an axial center void of 0.07-0.08 in. The maximum linear heating rate was about 19 kW/ft, and estimated temperatures for the specimen are 2670°C at the center-void surface and 1065°C at the outer surface of the fuel.

Electron-microprobe analysis[19] showed an unequivocal increase in plutonium content of the pin near the center (see Fig. 19). One could ascribe this effect to thermal diffusion and treat the fuel-pin data in the same fashion as the thermal-gradient experiments described above, assuming in this case a parabolic radial thermal gradient. The results of such a computation using a value of $\alpha = 7$ are shown in Fig. 19; this choice of α gave the best fit out of the various integers tried. The fit is reasonably good and could probably have been improved upon by a more refined choice of α.

Another possibility is that the central portion of the fuel pin may have been molten at some time. Assuming that the long columnar-grain region essentially represents the molten region, one can calculate a redistribution

of plutonium on freezing by means of "normal freezing" theory. Using a value of K = 0.679, based on the phase diagram and the size of the columnar-grain region, we obtained the distribution shown in Fig. 19. Again the agreement is reasonably good.
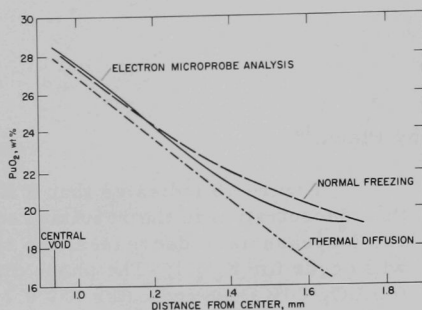

Fig. 19

Plutonium Redistribution in Irradiated Fuel Pin Initially 20 wt % PuO_2-UO_2. ANL Neg. No. 308-2283 Rev. 1.

Thus, a priori, one could not say which mechanism was operating in this fuel pin, but in most cases there are at least three possibilities:

1.   Selective vaporization

2.   Thermal diffusion

3.   Normal freezing.

For those pins that have been molten, normal freezing may be the most important mechanism; for those that have never been melted, selective vaporization could yield an apparent redistribution of plutonium toward the hot portion of the sample. Thermal diffusion may also be operative, but evidence for its action does not seem clear-cut at this time.

VII. CONCLUSIONS

Plutonium redistribution in a $(U_{0.8}Pu_{0.2})O_{2+x}$ sample (hyperstoichiometric) does appear to take place under the influence of a thermal gradient. A hypostoichiometric pellet did not show any significant redistribution. A possible mechanism for this behavior is selective vaporization of uranium from the hot end of the sample, chiefly by the UO_3 gaseous species. Thermal-diffusion effects, however, cannot be conclusively ruled out on the basis of these studies. In any event, the magnitude of the effect in our studies seems small.

Scouting experiments in which mixed-carbide pellets were maintained in thermal gradients similar to those for the oxides indicated that plutonium losses from the sample by vaporization could be considerable. However, addition of a metallic cladding to reduce vaporization sharply lowered plutonium losses to insignificant levels.

Restructuring of oxides and carbides under the influence of a thermal gradient was observed. Formation of columnar grains and enlargement of void size at the hotter end of the samples were typical.

In oxide specimens, losses and redistribution of oxygen occurred. Sampling techniques employed, however, were not sensitive enough to reveal much about the mechanism, although vaporization, thermal diffusion, and cladding interactions are probably important.

For samples that have been molten, redistribution of fissile material by the solidus-liquidus separation effect should be kept in mind as a possible mechanism.

ACKNOWLEDGMENTS

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